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# Microstructures of cast silver-copper alloy archaeological artefacts

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Cast silver-copper alloy objects form a significant part of the archaeological record of silver from at least the first millennium BC onwards but there has been little study of their microstructures. Wrought silver-copper alloys have been more extensively studied with a particular focus on the evidence for discontinuous precipitation of copper from supersaturated solid solution at ambient temperature over archaeological time and whether this could be used as an indicator or measure of age (see eg [1][2]). Studies of the cast alloys are hindered by the very fine scale of precipitation which forms within the grains over a broad range of cooling rates which challenges the resolving power of optical methods while there are significant experimental difficulties of determining orientation relationships using either X-ray methods or by transmission electron microscopy. The work presented here used a combination of scanning electron microscopy (SEM), electron backscattered diffraction (EBSD) and optical microscopy (OM) to explore the range of microstructures represented in cast silver from archaeological contexts and compare them with those observed in modern cast silver with the aim of both improving our understanding of precipitation in these alloys and of finding out if this can provide information on the age of the artefact

Silver-copper alloys are sensitive to the precipitation of copper because of the difference in its solid solubility between the typical annealing temperatures of up to 700°C (7%) and room temperature (<1%). Two particular types of precipitation are of interest; continuous and discontinuous (DP) (classified on the basis of transformation mechanism not morphology). There have been many studies of DP in pure binary Ag-Cu alloys, especially of growth rates at different temperatures mostly above 200°C (eg[3]). The DP commonly takes the form of 'colonies' of alternating lamellae of silver rich  $\alpha$  and copper rich  $\beta$  growing away from grain boundaries but at lower ageing temperatures the colonies often appeared finely mottled or structureless rather than lamellar. In pure binary alloys hardness measurements [4], differential scanning calorimetry [5][6] dilatometry[5] and resistivity measurements[6][7] have indicated the formation of two metastable ppts but no continuous  $\beta$  precipitation prior to DP.

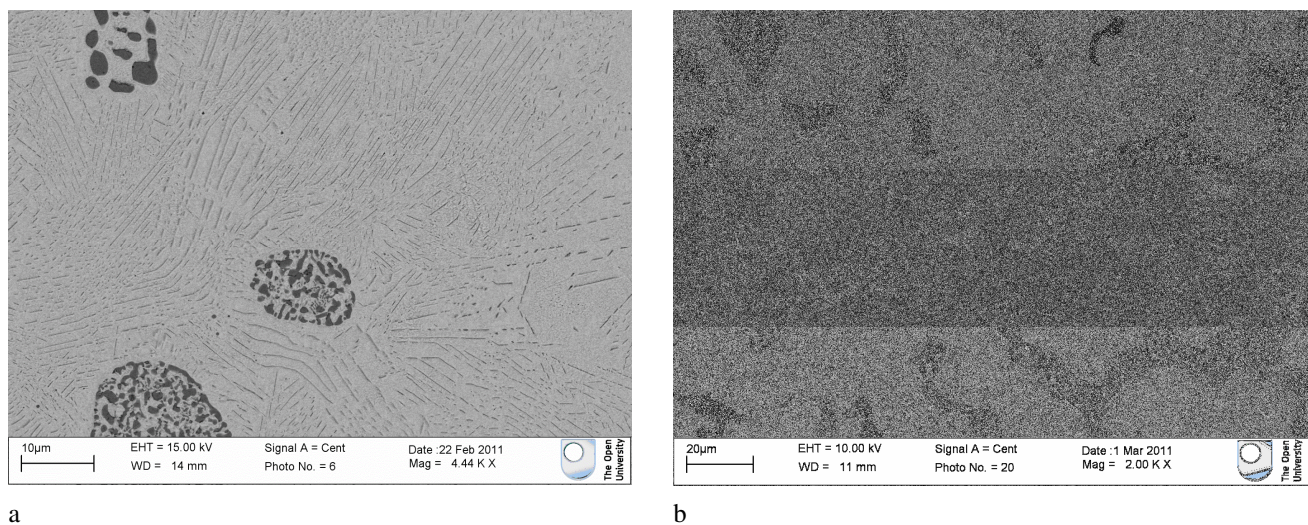
As shown in fig.1a, in modern cast sterling silver (Ag-7.5 wt%Cu) fine scale precipitation of copper can occur within the grains with a variety of morphologies, often in the form of very slender rods or laths, often bundled parallel, on occasion in a more radial array. They are observed optically only due to the trench excavated round them by the etch. The SEM is required to define their length and diameter accurately. They can be as little as 50nm in diameter and they tend to become separated from the silver matrix complicating the determination of orientation relationships. For EBSD the etch was minimised to that necessary to remove surface damage and this made the precipitates much easier to observe in the backscattered image. These precipitates are not themselves readily detectable with EBSD but EBSD does allow us to map the local orientation of all areas within the as-cast grains and, by comparison with the SEM images, begin to model the habit of the precipitates in relation to the matrix. Despite exhaustive observation there was no evidence of any connection between the precipitates and the copper rich  $\beta$  phase of the primary eutectic.

Ancient cast silver-copper alloy objects displayed a wide range of microstructures, some such as that from an Achaemenid period (6<sup>th</sup> -4<sup>th</sup> cent. BC Iran) beaker (fig.1b) very similar to that of modern cast silver but others such as that of a cast silver horses head of the same period (fig2) are quite different. The cast structure rather obscures the boundaries in optical, secondary electron or backscattered images but orientation images clearly show fine-scale interpenetration of the adjoining grains suggesting cellular growth. This suggests that over archaeological time boundary modification may take place in cast as well as wrought and annealed structures. Unlike the case of

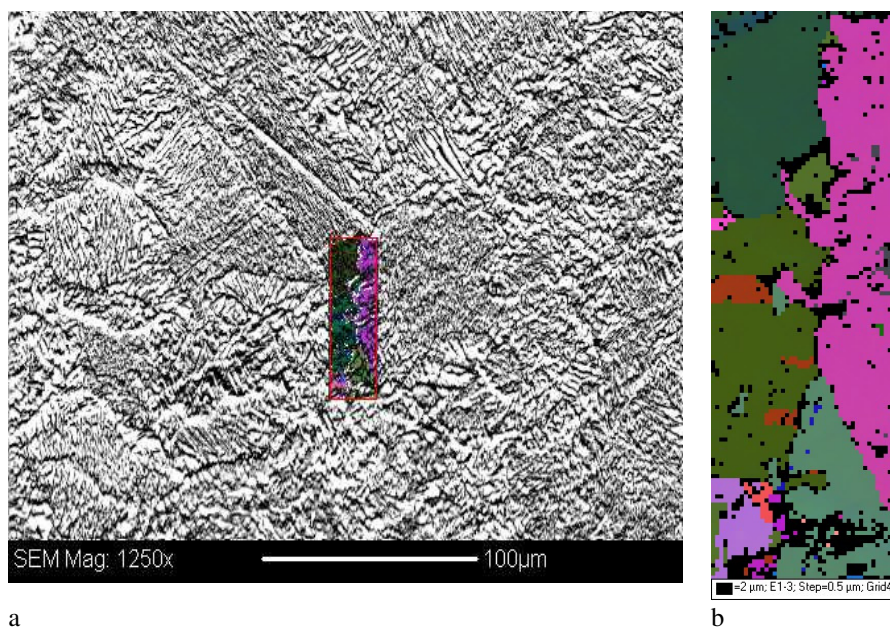
wrought and annealed material in which boundary modifications produced by short term high temperature ageing cannot be distinguished from those produced at ambient temperature over archaeological time, the simultaneous effects of any heat treatment on the intragranular precipitates of these cast microstructures might allow such a distinction. This will be a topic of further research.

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**Figure 1.** Backscattered electron SEM images of the microstructure of (a) modern cast sterling silver, (b) a cast silver beaker (6<sup>th</sup> -4<sup>th</sup> cent. BC)



**Figure 2.** Microstructure a cast silver horse's head (6<sup>th</sup> -4<sup>th</sup> cent. BC)  
(a) Secondary electron SEM image (b) EBSD map of the region of a grain boundary